

Chemically Synthesised Atomically Precise Gold Clusters

Deposited and Activated on Titania

David P. Anderson¹, Jason F. Alvino², Alexander Gentleman², Hassan Al Qahtani³,
Lars Thomsen⁴, Matthew I. J. Polson¹, Gregory F. Metha^{*2}, Vladimir B. Golovko^{*1}, and
Gunther G. Andersson^{*3}

Electronic supplementary information (ESI)

I. Preparation of the ligand stabilised gold cluster

All basic laboratory chemicals (solvents *etc.*, AR grade) have been purchased from established suppliers, (e.g. Sigma-Aldrich), and used without further purification. Evonik TiO₂ P-25 aerioxide (CAS-No 13463-67-7) was purchased from Chemiplas NZ. Tetrachloroauric acid was prepared using 99.99% pure gold following the procedure detailed by Brauer.¹ Unless otherwise specified, reactions have been carried out under air.

AuPPh₃(Cl) The synthesis protocol was adapted from the procedure described by Bruce *et al.*² Triphenylphosphine (2.65 g, 10.10 mmol) in ethanol (75 mL) was added rapidly to a stirred (500 rpm) solution of tetrachloroauric acid (2.010 g, 5.102 mmol) in ethanol (20 mL). The yellow colour of solution disappeared immediately upon addition of triphenylphosphine to form a white precipitate. The resulting solution was stirred vigorously (1000 rpm) for a further 15 minutes. The reaction mixture was centrifuged (5 min, 5000 rpm) and the white product collected, then washed 3 times with hot ethanol (3 × 20 mL) on a sintered glass funnel filter (porosity 3). The remaining solid was dissolved in chloroform (30 mL), filtered and the solvent removed under reduced pressure. The crude product was dried in a vacuum desiccator. The product was recrystallized from a mixture of dichloromethane and methanol using vapour diffusion resulting in needle-like white crystals.

Yield: 2.250 g, 90 %. ³¹P NMR (chloroform, 25 °C); δ 33.5 ppm referenced to H₃PO₄

AuPPh₃(NO₃) was synthesised according to a protocol described by Mueting *et al.*³ A solution of AgNO₃ (3.430g, 20.191 mmol) in ethanol (130 mL) was added rapidly to a solution of AuPPh₃(Cl) (3.973g, 8.042 mmol) in chloroform (50 mL). The reaction was left to stir for 1 hour with the reaction vessel covered with aluminium foil. The precipitate of AgCl was removed by filtering on a sintered glass funnel filter (porosity 3) and the filtrate was then dried in a rotary evaporator without heating. The crude product was washed with ethanol (3 × 50 mL). The solid was then dissolved in the dichloromethane (50 mL) to which ethanol

(150 mL) was added. The solution was then bubbled through with a flow of nitrogen for 2 hours to remove the dichloromethane. The resulting white crystals were collected by filtration, washed with cold ethanol (3×5 mL) and cold diethyl ether (3×5 mL). The product was stored in a freezer in the absence of light.

Yield: 3.648g, 87 %. ^{31}P NMR (chloroform, 25 °C); δ 25.2 ppm referenced to H_3PO_4

1.5 nm Au clusters, “Au₁₀₁” or $\text{Au}_{101}[\text{P}(\text{C}_6\text{H}_5)_3]_{21}\text{Cl}_5$ stabilized by triphenylphosphine were prepared according to a protocol described by Hutchison *et al.*^{4,4} Tetraoctylammonium bromide (1.40 g, 2.56 mmol) was added to a solution of tetrachloroauric acid (1 g, 2.54 mmol) in ultrapure water (60 mL) and toluene (60 mL). After 5 minutes of vigorous stirring at 1000 rpm, triphenylphosphine (2.3 g, 8.76 mmol) is added to the biphasic system. After 10 minutes of vigorous stirring, a solution of freshly dissolved sodium borohydride (2.0 g, 52.9 mmol) in ultrapure water was rapidly added to the reaction mixture. The reaction mixture was left to stir at 600 rpm for a further 3 hours, after which point the organic layer was separated and washed with saturated solution of NaCl in ultrapure water (2×50 mL) and then ultrapure water (3×50 mL). The organic layer was separated, filtered and dried under reduced pressure. The resulting solid was redissolved in chloroform (35 mL) to which pentane (300 mL) was added slowly with gentle swirling and the mixture allowed to stand overnight. The precipitate was collected by filtration on a sintered glass funnel filter (porosity 4) and washed with series of solvent mixtures as follows:

2 $\times$ 100 mL hexanes followed by 100 mL 2: 3 MeOH: H_2O)

2 $\times$ 100 mL hexanes followed by 100 mL 1: 1 MeOH: H_2O)

2 $\times$ 150 mL 3: 1 pentane: chloroform

2 $\times$ 150 mL 2: 1 pentane: chloroform

2 $\times$ 150 mL 1: 1 pentane: chloroform

The solvent washes are used to remove by-product $\text{AuPPh}_3(\text{Cl})$ and the phase transfer reagent. The effectiveness of the purification steps was monitored by ^1H NMR. The remaining solid was dissolved in dichloromethane (30 mL) and filtered through to recover the product. Removal of solvent under reduced pressure (rotary evaporator) afforded pure product as a fine black powder.

Yield: 200 – 250 mg.

This cluster was characterised by HRTEM (Fig. S1) and its purity was confirmed by ^1H NMR in CDCl_3

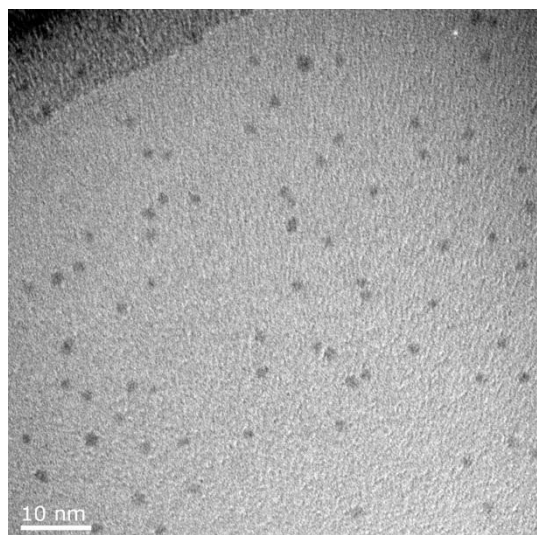


Figure SI 1: A representative HRTEM image of Au₁₀₁ particles deposited onto carbon film of TEM grid (obtained using Philips CM200 high resolution analytical transmission electron microscope).

Au₁₁(PPh₃)₈Cl₃ was synthesised according to a modified protocol described by Hutchison *et al.*^{5,6}

A solution of NaBH₄ (0.075 g, 1.97 mmol) in ethanol (5 mL) was added dropwise to a stirred suspension of Au(PPh₃)Cl (1.0 g, 2.02 mmol) in ethanol (50 mL). The reaction mixture was left to stir for 2 hours, after which time it was poured into hexanes (1 L) and the product was allowed to precipitate overnight. The precipitate was collected using a sintered glass filter funnel (porosity 4). It was then washed with hexanes (4 × 15 mL), 1:1 (v/v) mixture of CH₂Cl₂: hexanes (4 × 15 mL), and 3:1 (v/v) mixture of CH₂Cl₂: hexanes (1 × 10 mL). The solid remaining on the filter was dissolved in dichloromethane (20 mL) and filtered through to remove any insoluble by-products. The crude product was obtained upon removal of solvent in vacuum. It was recrystallized from a mixture of dichloromethane and diethyl ether by vapour diffusion at 4°C resulting in deep red platelets.

Yield: 155 mg, 17.5%

³¹P NMR (chloroform, 25 °C); δ 52.2 ppm referenced to H₃PO₄

Mass spectrometry (MS) was performed using Bruker maXis UHR-TOF MS with an electrospray ionisation (ESI) source and positive-ion polarity.

Isotopic distribution modelling was completed by the molecular weight calculator kindly distributed by PNNL <http://ncrr.pnl.gov/software/>

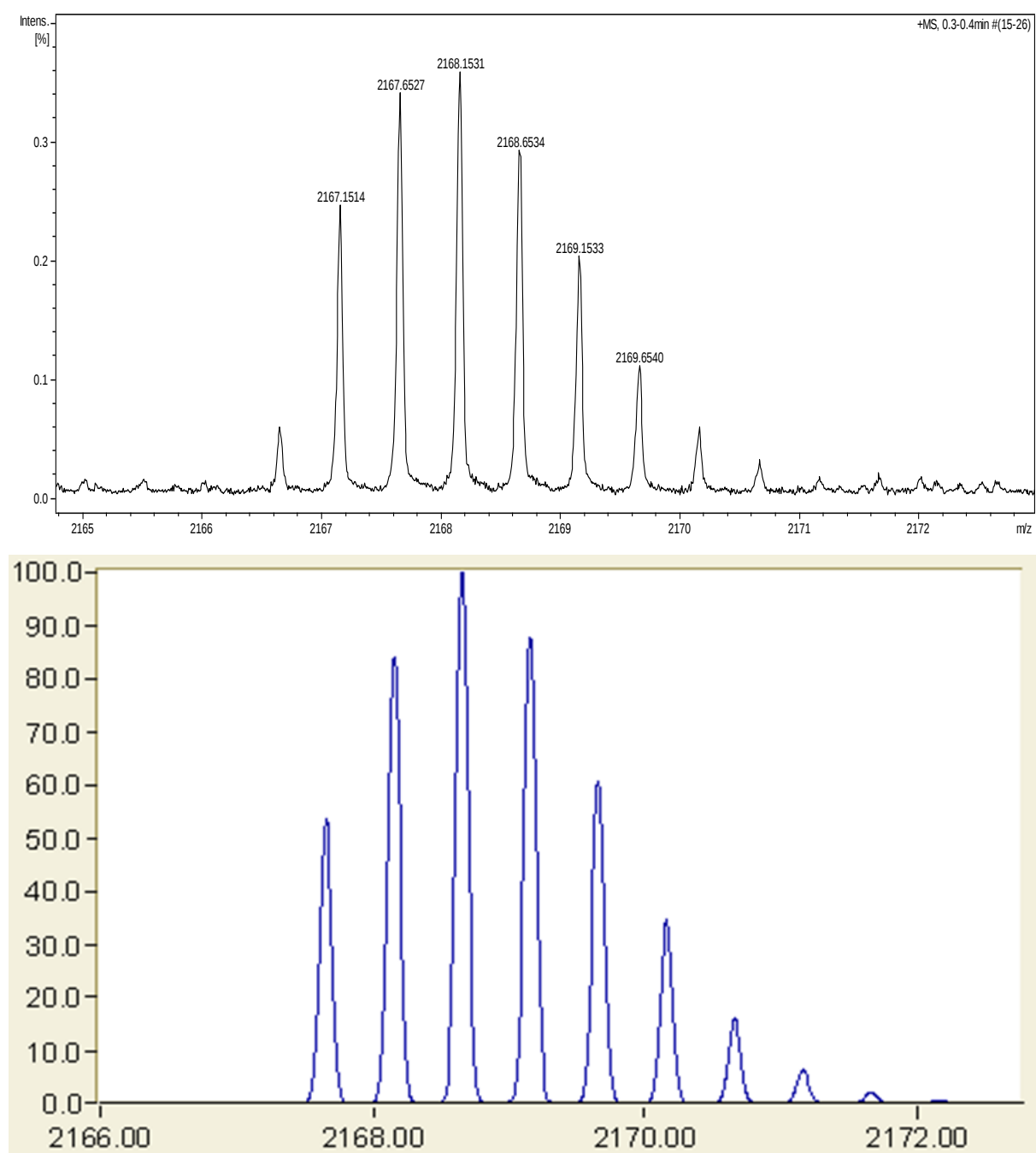


Figure SI 2: Top: Molecular ion peak for the $[\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^{2+}$, bottom: the isotopic distribution and simulated spectra pattern for the molecular ion.

Table SI 1: Values of m/z, fraction and intensity for the simulated high resolution MS for Au₁₁.

Mass/Charge	Fraction	Intensity
2167.657	0.119819	53.42
2168.157	0.18877	84.17
2168.657	0.224282	100
2169.157	0.197174	87.91
2169.657	0.136167	60.71
2170.157	0.077238	34.44
2170.657	0.036252	16.16
2171.157	0.014096	6.28
2171.657	0.004576	2.04
2172.157	0.001257	0.56
2172.657	0.000298	0.13
2173.157	6.05E-05	0.03
2173.657	1.22E-05	0.01
2174.157	1.6E-06	0

Au₉(PPh₃)₈(NO₃)₃ was synthesised following protocol described by Wen *et al.*⁷

A solution of NaBH₄ (0.072 g, 1.92 mmol) in ethanol (92 mL) was added to the magnetically stirred solution of AuPPh₃(NO₃) (4.0 g, 7.6 mmol) in ethanol (160 mL). The solution became deep red within two hours, after which point the solution was filtered to remove insoluble impurities and solvent removed *in vacuo*. The solid obtained was dissolved in 20 mL CH₂Cl₂ and filtered through sintered glass filter funnel (porosity 3). Removal of solvent on rotary evaporator yield product as black precipitate, which was washed with 50 mL of THF. Upon washing, the solid becomes dark-green. The solid was further washed with THF (3 x 50 ml) and hexanes (3 x 50 ml). The precipitate was crystallized from a methanol solution by slow diffusion of diethyl ether at 4°C. Dark green crystals formed within ca. 5 days.

Yield 1.24 g, 36 %.

³¹P NMR (chloroform, 25 °C); δ 56.8 ppm referenced to H₃PO₄

Mass spectrometry (MS) was performed using Bruker maXis UHR-TOF MS with an electrospray ionisation (ESI) source and positive-ion polarity.

Isotopic distribution modelling was completed by the molecular weight calculator kindly distributed by PNNI <http://ncrr.pnl.gov/software/>

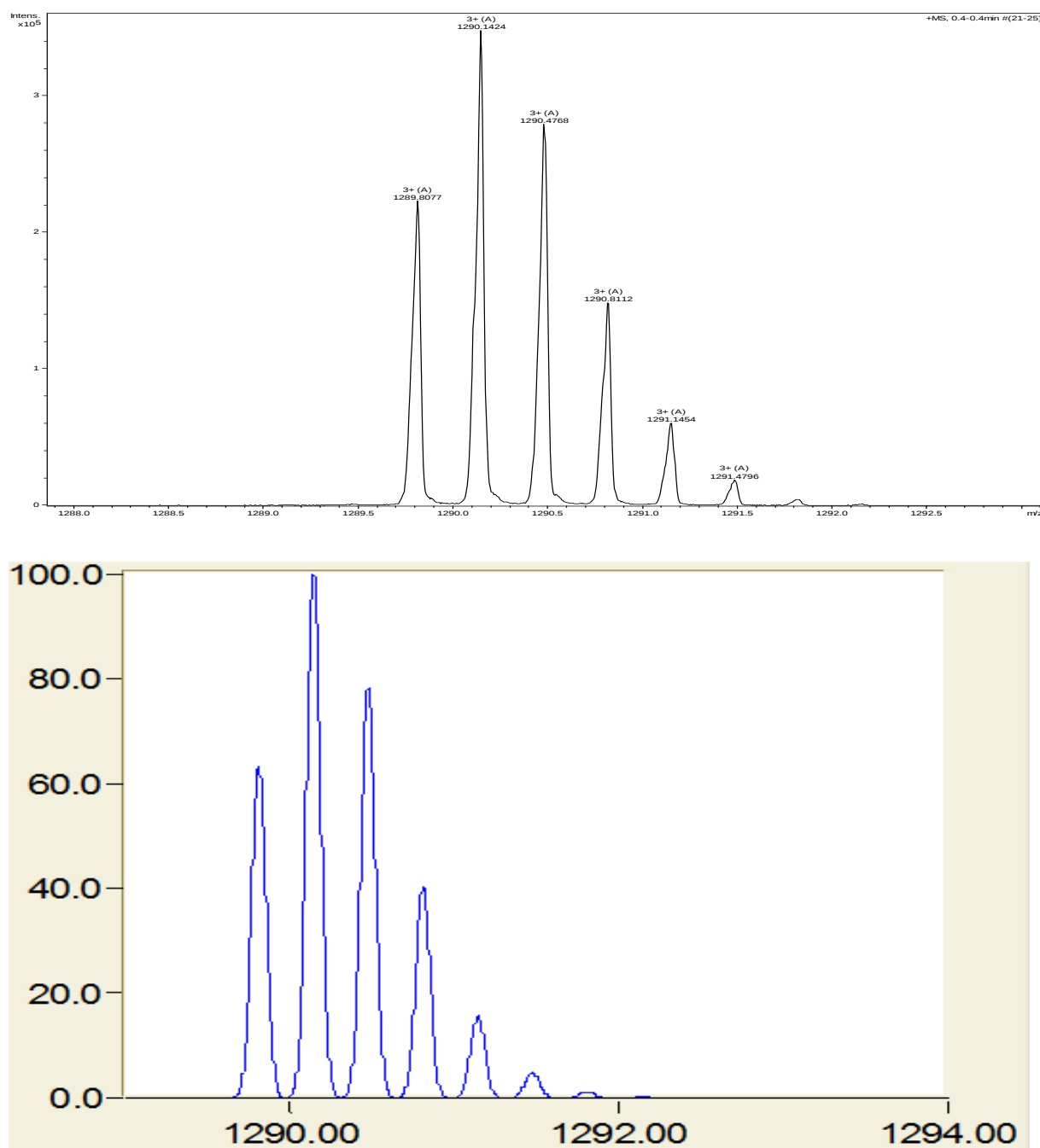


Figure SI 3: Top: Molecular ion peak for the $[\text{Au}_9(\text{PPh}_3)_8]^{3+}$, bottom: the isotopic distribution and simulated spectra pattern for the molecular ion.

Table SI 2: Values of m/z, fraction and intensity for the simulated high resolution MS for Au₉.

Mass/Charge	Fraction	Intensity
1289.80877	0.2087423	63.49
1290.1421	0.3287728	100
1290.47543	0.257153	78.22
1290.80877	0.1331733	40.51
1291.1421	0.0513696	15.62
1291.47543	0.0157422	4.79
1291.80877	0.0039922	1.21
1292.1421	0.0008617	0.26
1292.47543	0.0001616	0.05
1292.80877	0.0000267	0.01
1293.1421	0.0000075	0

Au₈(PPh₃)₈(NO₃)₂ was synthesised following the protocol described by Van der Velden *et al.*

8

[Au₉(PPh₃)₈](NO₃)₃ (1.48 g, 0.36 mmol) and PPh₃ (0.96 g, 3.66 mmol, 10-fold excess) were mixed in 20 mL of CH₂Cl₂. The resulting deep red solution was stirred a further 30 minutes. After that the red product was precipitated by addition of 200 mL of toluene, isolated by filtration on a glass frit (porosity 3), washed alternately with toluene (3 x 20 mL) and hot hexanes (3 x 20 mL) and dried. The red product was crystallized from CH₂Cl₂ solution by slow diffusion of diethyl ether at 4°C. Deep red crystals formed within ca. 4 days. The crystallization was repeated several times to remove excess of triphenylphosphine.

Yield: 1.38 g, 88 %.

³¹P NMR (chloroform, 25 °C); δ 58.2 ppm referenced to H₃PO₄

Mass spectrometry (MS) was performed using Bruker maXis UHR-TOF MS with an electrospray ionisation (ESI) source and positive-ion polarity.

Isotopic distribution modelling was completed by the molecular weight calculator kindly distributed by PNNI <http://ncrr.pnl.gov/software/>

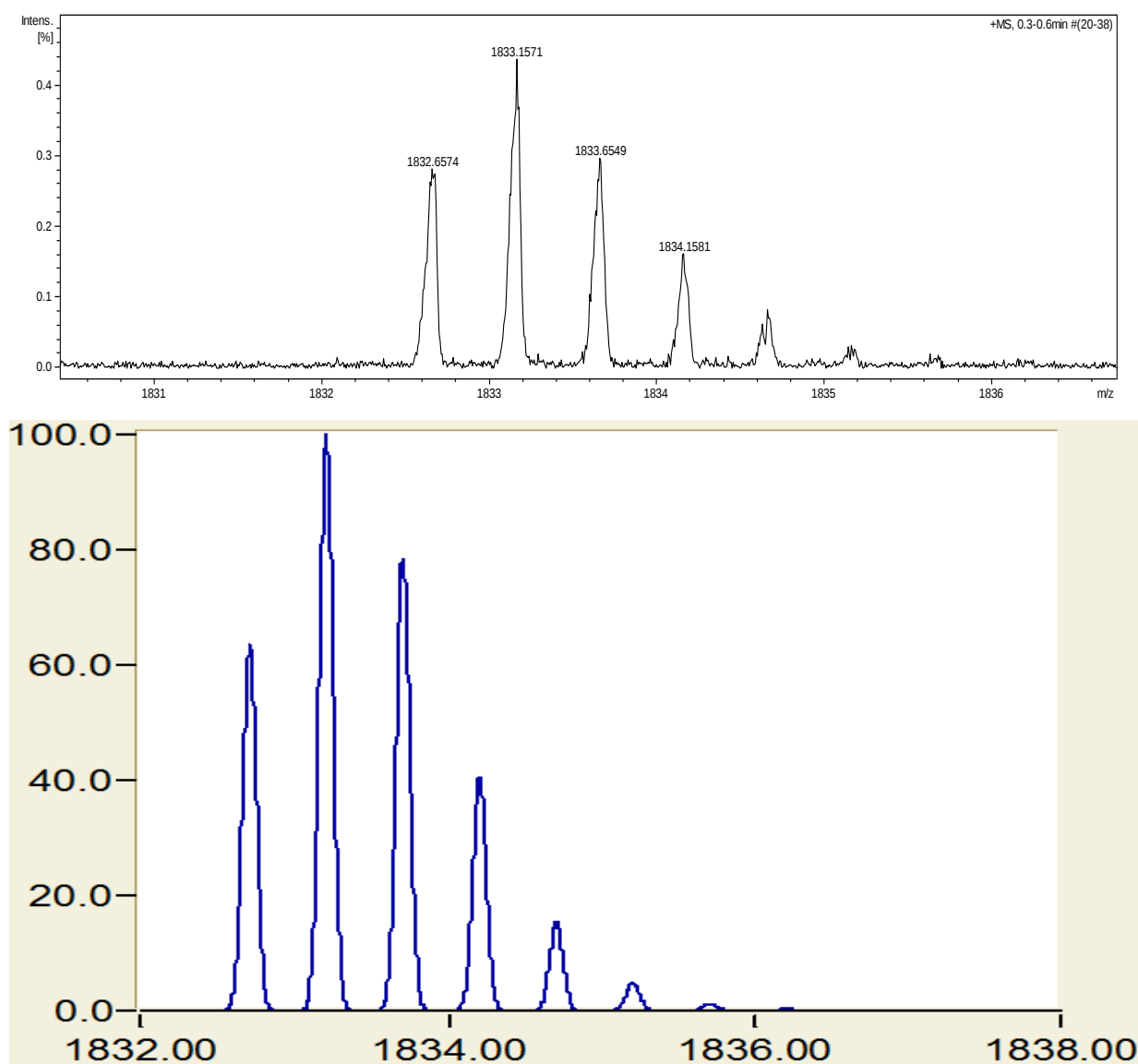


Figure SI 4: Top: Molecular ion peak for the $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$, bottom: the isotopic distribution and simulated spectra pattern for the molecular ion.

Mass/Charge	Fraction	Intensity
1832.703	0.20893	63.53
1833.203	0.328881	100
1833.703	0.257089	78.17
1834.203	0.133062	40.46
1834.703	0.051296	15.6
1835.203	0.01571	4.78
1835.703	0.003982	1.21
1836.203	0.000859	0.26
1836.703	0.000161	0.05
1837.203	2.66E-05	0.01

Table SI 3: Values of

1837.703	7.4E-06	0
----------	---------	---

 m/z, fraction and intensity for the simulated high resolution MS for Au₈.

Acid washed Evonik P-25 TiO₂ was fabricated following the protocol described by Lopez-Sanchez *et al*⁹ Evonik P-25 TiO₂ (ca. 10 g) was acid washed with aqueous H₂SO₄ (1 mol/L, 100 ml) with stirring (600 rpm) over 5 hours. The solid was separated by centrifugation (10 min, 5000 rpm). It was then washed with distilled water (50 ml) and methanol (50 ml) by forming a suspension using a Vortex agitator followed by centrifugation (10 min, 5000 rpm) to recover the solid each time. Finally, washed TiO₂ was dried at 100 °C under vacuum for 4 hours.

II. Preparation of the reference samples and recording of the reference spectra

Samples for measuring photoelectron reference spectra of each gold cluster were prepared by drop casting two droplets from a 1 mg/cm³ isopropanol solution of the Au_n cluster on a silicon wafer covered with 10 nm of atomic layer deposited titania. The solution was left drying in air. The photoelectron spectra of the reference samples were recorded using a non-monochromatic Mg-Kα radiation and a Phoibos 100 electron energy analyser from SPECS in a vacuum chamber with a base pressure of a few 10⁻¹⁰ mbar.

III. Normalisation of the gold intensity

The gold signal was normalised against the silicon dioxide signal according to

$$I_{\text{Au}}^{\text{norm}} = I_{\text{Au}} / \left(1 - \left(I_{\text{Si,Si}} + I_{\text{Si,SiO}_2} + I_{\text{O,SiO}_2} \right) \right) \quad \text{Eq. 1}$$

where $I_{\text{Au}}^{\text{norm}}$ is the normalised gold intensity, I_{Au} is the relative gold intensity, $I_{\text{Si,Si}}$ the relative intensity of silicon of the silicon substrate, $I_{\text{Si,SiO}_2}$ the relative intensity of silicon in the native

SiO₂ layer at the surface of Si wafers and I_{O, SiO_2} the relative intensity of oxygen of the silicon dioxide layer covering the silicon substrate. Relative intensity means the intensity of the respective element is normalised by its photo-ionisation cross section and divided by the sum of the intensities of all elements detected. Thus $(I_{Si, Si} + I_{Si, SiO_2} + I_{O, SiO_2})$ represents the fraction of the sample not covered by titania particles and $(1 - (I_{Si, Si} + I_{Si, SiO_2} + I_{O, SiO_2}))$. The fraction of the surface covered by titania particles. The uncertainty of the normalisation procedure is the largest contribution to the error bar of the gold intensity in **Error! Reference source not found.**

IV. Relative intensity of the phosphorous spectra

For the quantitative analysis of the phosphorous intensity only the phosphorous to gold ratio has been considered. The ratio is calculated as

$$I_{P-Au}^{ratio} = I_P / I_{Au} \quad \text{Eq. 2}$$

where I_{P-Au}^{ratio} is the phosphorous to gold ratio, I_P is the phosphorous intensity and I_{Au} the gold intensity.

V. Fitting of the Au₉ spectra

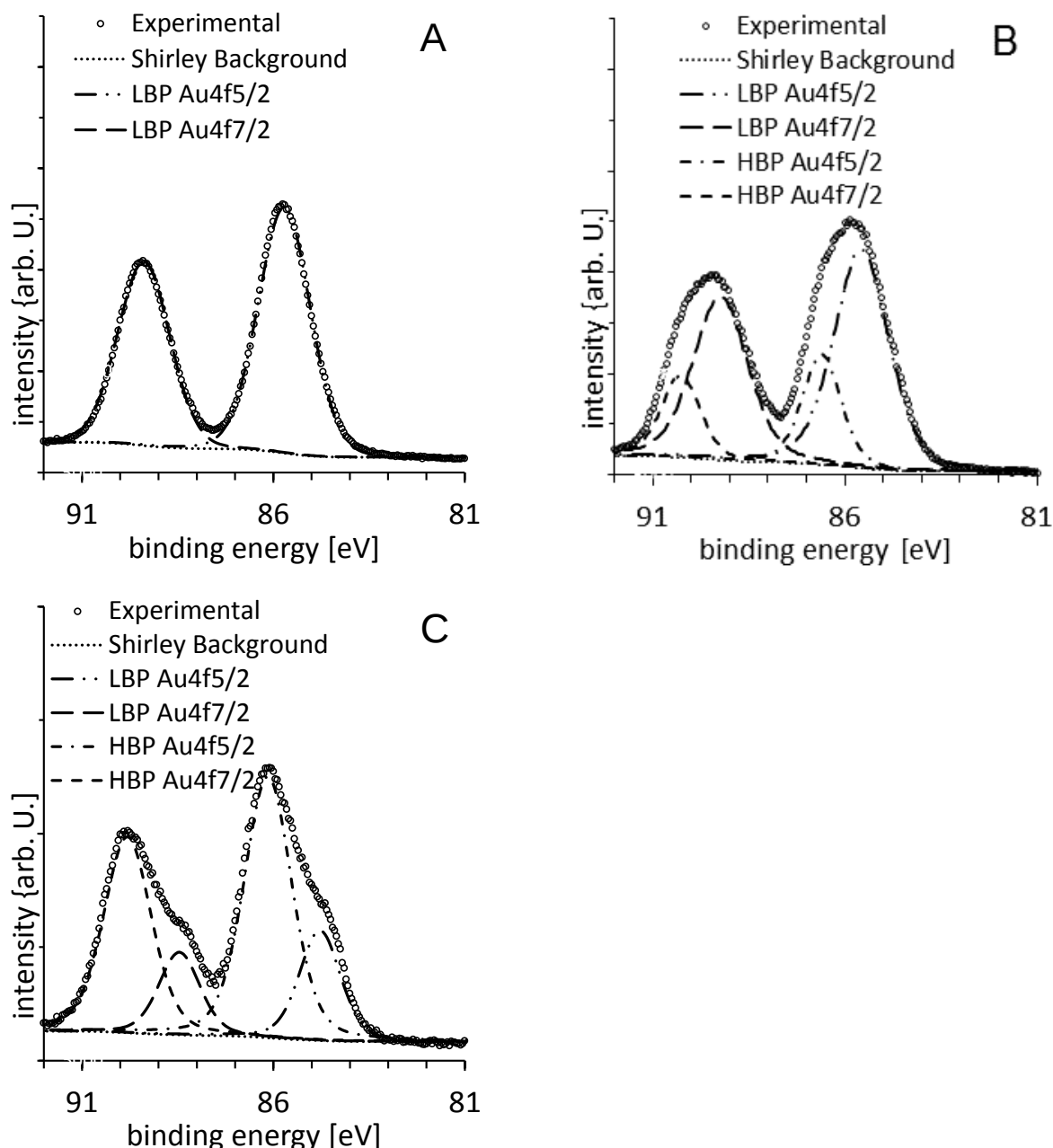


Figure SI 5: fit of the Au₉ spectra. A) untreated clusters, B) washed clusters and C) calcined clusters.

VI. Structure Determination for Au₈ and Au₁₁ clusters

X-Ray crystal data was collected on a Bruker-Nonius APEX II system using graphite monochromatised Mo Ka ($\lambda = 0.71073 \text{ \AA}$) radiation. The crystals were kept at 113 K during data collection. The data collection, cell determination and data reduction were all performed with the APEX software. All structures had intensities corrected for Lorentz and polarisation effects and for absorption using SAINT. Absorption corrections were made using SADABS. All structures were solved by direct methods using the XS¹⁰ structure solution program and

refined on F2 using all data by full-matrix least squares procedures using and using Olex2¹¹, it was refined with the XH¹⁰ refinement package using Least Squares minimisation. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed as riding atoms with displacement parameters 1.2 times the isotropic equivalent of their carrier carbon atoms. Details of the structures are available from Cambridge Crystallographic Database (CCDC) under reference numbers 907704 for Au₁₁ and 907703 for Au₈.

Au₁₁ Crystal Data. C_{144.5}H₁₂₁Au₁₁Cl₄P₈, *M* = 4413.60, monoclinic, *a* = 22.5484(8) Å, *b* = 18.1152(6) Å, *c* = 34.6185(12) Å, β = 95.997(2)°, *V* = 14063.2(8) Å³, *T* = 113, space group P2₁/c (no. 14), *Z* = 4, μ(Mo Kα) = 11.640, 244873 reflections measured, 24902 unique (*R*_{int} = 0.1616) which were used in all calculations. The final *wR*₂ was 0.1612 (all data) and *R*₁ was 0.0570 (>2σ(*I*)).

In the Au₁₁ structure similar issues were seen with the phenyl rings, again giving spurious Hirshfeld difference warnings and poor C-C bond accuracies. The counter ion chloride (as opposed to the covalently bound chlorides which were well behaved) was equally disordered over four sites. A half molecule of dichloromethane was also included in the structure.

Au₈ Crystal Data. C₁₄₈H₁₂₈N₂O₆P₈Au₈Cl₈, *M* = 4137.62, triclinic, *a* = 16.8008(5) Å, *b* = 17.0945(5) Å, *c* = 28.2942(10) Å, α = 83.338(2)°, β = 84.698(2)°, γ = 62.656(2)°, *V* = 7162.4(4) Å³, *T* = 113, space group P-1 (no. 2), *Z* = 2, μ(Mo Kα) = 8.453, 96342 reflections measured, 25320 unique (*R*_{int} = 0.1170) which were used in all calculations. The final *wR*₂ was 0.1447 (all data) and *R*₁ was 0.0634 (>2σ(*I*)).

In the Au₈ structure, four molecules of dichloromethane were disordered over five sites. Both nitrate anions were poorly ordered with the second nitrate requiring significant restraints. The phenyl rings of the phosphine ligands tend to move in the plane of the ring, meaning the thermal ellipsoids are elongated along some of the bonds. This leads to spurious Hirshfeld difference warnings (that the thermal ellipsoids are elongated towards another atom)¹² and poor C-C bond accuracies.

Table SI 4: Crystal data and structure refinement for Au₈(PPh₃)₈(NO₃)₂·4CH₂Cl₂ and Au₁₁(PPh₃)₈Cl₃·0.5CH₂Cl₂

Empirical formula	C _{144.5} H ₁₂₁ Au ₁₁ Cl ₄ P ₈	C ₁₄₈ H ₁₂₈ N ₂ O ₆ P ₈ Au ₈ Cl ₈
Formula weight	4413.60	4137.62
Temperature/K	113 (2)	113 (2)
Crystal system	monoclinic	triclinic
Space group	P2 ₁ /c	P-1

a/Å	22.5484(8)	16.8008(5)
b/Å	18.1152(6)	17.0945(5)
c/Å	34.6185(12)	28.2942(10)
α/°	90.00	83.338(2)
β/°	95.997(2)	84.698(2)
γ/°	90.00	62.656(2)
Volume/Å ³	14063.2(8)	7162.4(4)
Z	4	2
ρ _{calc} /mg/mm ³	2.085	1.919
m/mm ⁻¹	11.640	8.453
F(000)	8180.0	3932.0
Crystal size/mm ³	0.40 × 0.25 × 0.02	0.31 × 0.21 × 0.2
2Θ range for data collection	4.34 to 50.1°	3.14 to 50.1°
Index ranges	-26 ≤ h ≤ 26, -21 ≤ k ≤ 21, -41 ≤ l ≤ 41	-18 ≤ h ≤ 20, -19 ≤ k ≤ 20, -33 ≤ l ≤ 33
Reflections collected	244873	96342
Independent reflections	24902[R(int) = 0.1616]	25320[R(int) = 0.1170]
Data/restraints/parameters	24902/66/1549	25320/145/1675
Goodness-of-fit on F ²	1.024	0.946
Final R indexes [I>=2σ (I)]	R ₁ = 0.0570, wR ₂ = 0.1319	R ₁ = 0.0634, wR ₂ = 0.1305
Final R indexes [all data]	R ₁ = 0.1329, wR ₂ = 0.1614	R ₁ = 0.1241, wR ₂ = 0.1447
Largest diff. peak/hole / e Å ⁻³	3.30/-3.03	3.31/-2.14

Table SI 5: Bond Lengths for Au₁₁

Atom Atom Length/Å			Atom Atom Length/Å		
Au1	Au2	2.7075(9)	P7	C67	1.83(2)
Au1	Au3	2.7199(9)	C55	C56	1.30(3)
Au1	Au4	2.7312(10)	C55	C60	1.38(3)
Au1	Au5	2.7067(10)	C56	C57	1.39(3)
Au1	Au6	2.6919(9)	C57	C58	1.39(3)
Au1	Au7	2.7055(9)	C58	C59	1.43(3)
Au1	Au8	2.6511(10)	C59	C60	1.35(3)
Au1	Au9	2.6437(9)	C61	C62	1.40(2)
Au1	Au10	2.6814(9)	C61	C66	1.38(3)
Au1	Au11	2.6906(9)	C62	C63	1.37(3)
Au2	Au3	2.8870(9)	C63	C64	1.35(3)
Au2	Au4	2.8816(9)	C64	C65	1.38(3)
Au2	Au5	3.0334(10)	C65	C66	1.37(3)

Au2	Au6	2.9810(10)	C67	C68	1.42(3)
Au2	Au7	3.0243(10)	C67	C72	1.36(3)
Au2	P2	2.270(5)	C68	C69	1.40(3)
Au3	Au4	2.8445(10)	C69	C70	1.37(3)
Au3	Au7	2.8904(10)	C70	C71	1.42(4)
Au3	Au9	2.8942(10)	C71	C72	1.36(3)
Au3	Cl3	2.353(5)	P8	C73	1.79(2)
Au4	Au5	2.9064(10)	P8	C79	1.851(19)
Au4	Au10	2.8586(10)	P8	C85	1.836(18)
Au4	P4	2.286(5)	C73	C74	1.41(3)
Au5	Au6	2.9470(10)	C73	C78	1.35(2)
Au5	Au10	3.1479(10)	C74	C75	1.42(3)
Au5	Au11	2.9447(11)	C75	C76	1.38(3)
Au5	Cl5	2.361(5)	C76	C77	1.39(3)
Au6	Au7	3.0043(10)	C77	C78	1.40(3)
Au6	Au8	3.3647(10)	C79	C80	1.40(3)
Au6	Au11	3.0735(10)	C79	C84	1.38(3)
Au6	P6	2.298(5)	C80	C81	1.37(3)
Au7	Au8	2.9545(10)	C81	C82	1.44(3)
Au7	P7	2.312(5)	C82	C83	1.36(3)
Au8	Au9	3.1274(10)	C83	C84	1.42(3)
Au8	Au11	2.9026(10)	C85	C86	1.34(3)
Au8	P8	2.297(6)	C85	C90	1.39(3)
Au9	Au10	3.0465(10)	C86	C87	1.43(3)
Au9	P9	2.300(5)	C87	C88	1.35(3)
Au10	Au11	2.8637(10)	C88	C89	1.34(3)
Au10	P10	2.297(5)	C89	C90	1.40(3)
Au11	P11	2.298(4)	P9	C91	1.82(2)
P2	C1	1.835(19)	P9	C97	1.81(2)
P2	C7	1.83(2)	P9	C103	1.81(2)
P2	C13	1.832(18)	C91	C92	1.41(3)

C1	C2	1.35(3)	C91	C96	1.41(3)
C1	C6	1.40(3)	C92	C93	1.48(4)
C2	C3	1.39(3)	C93	C94	1.38(4)
C3	C4	1.38(3)	C94	C95	1.38(4)
C4	C5	1.33(3)	C95	C96	1.39(4)
C5	C6	1.40(3)	C97	C98	1.33(3)
C7	C8	1.38(3)	C97	C102	1.43(3)
C7	C12	1.37(2)	C98	C99	1.40(3)
C8	C9	1.37(3)	C99	C100	1.36(3)
C9	C10	1.43(3)	C100	C101	1.36(4)
C10	C11	1.35(3)	C101	C102	1.35(3)
C11	C12	1.40(3)	C103	C104	1.38(3)
C13	C14	1.37(2)	C103	C108	1.41(3)
C13	C18	1.38(2)	C104	C105	1.39(3)
C14	C15	1.38(3)	C105	C106	1.42(3)
C15	C16	1.40(3)	C106	C107	1.35(3)
C16	C17	1.37(3)	C107	C108	1.42(3)
C17	C18	1.41(2)	P10	C109	1.82(2)
P4	C19	1.801(18)	P10	C115	1.842(17)
P4	C25	1.842(17)	P10	C121	1.823(18)
P4	C31	1.822(19)	C109	C110	1.35(2)
C19	C20	1.35(2)	C109	C114	1.38(3)
C19	C24	1.46(3)	C110	C111	1.36(3)
C20	C21	1.43(3)	C111	C112	1.36(3)
C21	C22	1.34(3)	C112	C113	1.41(3)
C22	C23	1.37(3)	C113	C114	1.35(3)
C23	C24	1.40(3)	C115	C116	1.37(2)
C25	C26	1.39(2)	C115	C120	1.37(3)
C25	C30	1.35(3)	C116	C117	1.41(3)
C26	C27	1.42(3)	C117	C118	1.36(3)
C27	C28	1.32(3)	C118	C119	1.39(3)

C28	C29	1.35(3)	C119	C120	1.38(3)
C29	C30	1.40(3)	C121	C122	1.31(3)
C31	C32	1.32(3)	C121	C126	1.40(3)
C31	C36	1.40(3)	C122	C123	1.36(4)
C32	C33	1.40(3)	C123	C124	1.38(4)
C33	C34	1.37(3)	C124	C125	1.43(4)
C34	C35	1.37(3)	C125	C126	1.35(3)
C35	C36	1.37(3)	P11	C127	1.87(2)
P6	C37	1.814(19)	P11	C133	1.807(19)
P6	C43	1.832(19)	P11	C139	1.818(18)
P6	C49	1.802(19)	C127	C128	1.39(3)
C37	C38	1.35(2)	C127	C132	1.34(3)
C37	C42	1.37(2)	C128	C129	1.41(3)
C38	C39	1.41(3)	C129	C130	1.35(3)
C39	C40	1.39(3)	C130	C131	1.40(3)
C40	C41	1.40(3)	C131	C132	1.39(3)
C41	C42	1.41(3)	C133	C134	1.41(3)
C43	C44	1.35(3)	C133	C138	1.37(3)
C43	C48	1.39(3)	C134	C135	1.45(3)
C44	C45	1.36(3)	C135	C136	1.38(3)
C45	C46	1.37(4)	C136	C137	1.40(3)
C46	C47	1.37(4)	C137	C138	1.37(3)
C47	C48	1.38(3)	C139	C140	1.38(2)
C49	C50	1.37(3)	C139	C144	1.39(3)
C49	C54	1.42(3)	C140	C141	1.36(3)
C50	C51	1.41(3)	C141	C142	1.36(3)
C51	C52	1.34(3)	C142	C143	1.37(3)
C52	C53	1.42(3)	C143	C144	1.39(3)
C53	C54	1.40(3)	C500	Cl50	1.59(5)
P7	C55	1.825(19)	C500	Cl51	1.53(5)
P7	C61	1.858(18)			

Table SI 6: Bond Angles for Au₁₁.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Au2	Au1	Au3	64.27(3)	C9	C8	C7	123.1(18)
Au2	Au1	Au4	63.99(3)	C8	C9	C10	117.0(18)
Au3	Au1	Au4	62.91(3)	C11	C10	C9	120.0(18)
Au5	Au1	Au2	68.15(3)	C10	C11	C12	120.8(19)
Au5	Au1	Au3	120.02(3)	C7	C12	C11	119.7(19)
Au5	Au1	Au4	64.62(3)	C14	C13	P2	117.8(14)
Au6	Au1	Au2	67.02(3)	C14	C13	C18	120.2(17)
Au6	Au1	Au3	120.82(3)	C18	C13	P2	122.0(14)
Au6	Au1	Au4	119.77(3)	C13	C14	C15	118.9(19)
Au6	Au1	Au5	66.17(3)	C14	C15	C16	122(2)
Au6	Au1	Au7	67.64(3)	C17	C16	C15	119.1(19)
Au7	Au1	Au2	67.93(3)	C16	C17	C18	118.9(18)
Au7	Au1	Au3	64.38(3)	C13	C18	C17	120.7(17)
Au7	Au1	Au4	119.49(3)	C19	P4	Au4	109.7(6)
Au7	Au1	Au5	125.26(3)	C19	P4	C25	102.9(7)
Au8	Au1	Au2	130.58(3)	C19	P4	C31	110.7(8)
Au8	Au1	Au3	111.11(3)	C25	P4	Au4	117.4(6)
Au8	Au1	Au4	162.08(3)	C31	P4	Au4	113.3(7)
Au8	Au1	Au5	127.35(3)	C31	P4	C25	102.1(9)
Au8	Au1	Au6	78.06(3)	C20	C19	P4	122.6(14)
Au8	Au1	Au7	66.94(3)	C20	C19	C24	116.1(17)
Au8	Au1	Au10	105.15(3)	C24	C19	P4	121.2(14)
Au8	Au1	Au11	65.82(3)	C19	C20	C21	124(2)
Au9	Au1	Au2	129.44(3)	C22	C21	C20	118(2)
Au9	Au1	Au3	65.29(3)	C21	C22	C23	122(2)
Au9	Au1	Au4	90.12(3)	C22	C23	C24	120(2)
Au9	Au1	Au5	140.24(3)	C23	C24	C19	119.3(19)
Au9	Au1	Au6	149.51(4)	C26	C25	P4	116.8(13)
Au9	Au1	Au7	93.45(3)	C30	C25	P4	121.4(14)

Au9	Au1	Au8	72.41(3)	C30	C25	C26	121.8(17)
Au9	Au1	Au10	69.79(3)	C25	C26	C27	116.5(18)
Au9	Au1	Au11	103.95(3)	C28	C27	C26	122(2)
Au10	Au1	Au2	123.53(3)	C27	C28	C29	120(2)
Au10	Au1	Au3	107.66(3)	C28	C29	C30	121(2)
Au10	Au1	Au4	63.75(3)	C25	C30	C29	119(2)
Au10	Au1	Au5	71.49(3)	C32	C31	P4	125.6(16)
Au10	Au1	Au6	126.70(3)	C32	C31	C36	117.0(19)
Au10	Au1	Au7	163.19(3)	C36	C31	P4	117.0(14)
Au10	Au1	Au11	64.43(3)	C31	C32	C33	122(2)
Au11	Au1	Au2	126.20(3)	C34	C33	C32	119(2)
Au11	Au1	Au3	168.94(3)	C35	C34	C33	121(2)
Au11	Au1	Au4	116.50(3)	C34	C35	C36	118(2)
Au11	Au1	Au5	66.13(3)	C35	C36	C31	123(2)
Au11	Au1	Au6	69.64(3)	C37	P6	Au6	114.3(6)
Au11	Au1	Au7	120.91(3)	C37	P6	C43	101.2(9)
Au1	Au2	Au3	58.07(2)	C43	P6	Au6	115.6(6)
Au1	Au2	Au4	58.41(2)	C49	P6	Au6	114.2(7)
Au1	Au2	Au5	55.91(2)	C49	P6	C37	105.5(8)
Au1	Au2	Au6	56.24(2)	C49	P6	C43	104.6(10)
Au1	Au2	Au7	56.00(2)	C38	C37	P6	120.3(14)
Au3	Au2	Au5	105.07(3)	C38	C37	C42	116.1(18)
Au3	Au2	Au6	106.63(3)	C42	C37	P6	123.6(16)
Au3	Au2	Au7	58.49(2)	C37	C38	C39	123.5(18)
Au4	Au2	Au3	59.09(2)	C40	C39	C38	119(2)
Au4	Au2	Au5	58.79(2)	C39	C40	C41	119(2)
Au4	Au2	Au6	106.29(3)	C40	C41	C42	117.6(18)
Au4	Au2	Au7	105.32(3)	C37	C42	C41	124(2)
Au6	Au2	Au5	58.67(2)	C44	C43	P6	125.5(16)
Au6	Au2	Au7	60.03(2)	C44	C43	C48	120.5(18)
Au7	Au2	Au5	105.01(3)	C48	C43	P6	113.6(17)

P2	Au2	Au1	176.14(13)	C43	C44	C45	123(2)
P2	Au2	Au3	122.63(12)	C44	C45	C46	117(2)
P2	Au2	Au4	118.25(13)	C45	C46	C47	122(2)
P2	Au2	Au5	121.12(12)	C46	C47	C48	120(2)
P2	Au2	Au6	125.20(12)	C47	C48	C43	118(2)
P2	Au2	Au7	127.83(13)	C50	C49	P6	124.1(17)
Au1	Au3	Au2	57.66(2)	C50	C49	C54	116.7(18)
Au1	Au3	Au4	58.74(2)	C54	C49	P6	119.1(14)
Au1	Au3	Au7	57.57(2)	C49	C50	C51	124(2)
Au1	Au3	Au9	56.08(2)	C52	C51	C50	118(2)
Au2	Au3	Au7	63.13(2)	C51	C52	C53	122(2)
Au2	Au3	Au9	113.65(3)	C54	C53	C52	118(2)
Au4	Au3	Au2	60.36(2)	C55	P7	Au7	113.6(6)
Au4	Au3	Au7	109.94(3)	C55	P7	C61	102.9(8)
Au4	Au3	Au9	83.06(3)	C55	P7	C67	108.2(9)
Au7	Au3	Au9	84.65(3)	C61	P7	Au7	112.5(6)
Cl3	Au3	Au1	178.19(14)	C67	P7	Au7	117.6(6)
Cl3	Au3	Au2	120.73(14)	C67	P7	C61	100.3(8)
Cl3	Au3	Au4	121.54(16)	C53	C54	C49	120.9(19)
Cl3	Au3	Au7	121.25(15)	C56	C55	P7	118.6(14)
Cl3	Au3	Au9	125.58(14)	C56	C55	C60	118.5(19)
Au1	Au4	Au2	57.61(2)	C60	C55	P7	122.7(17)
Au1	Au4	Au3	58.35(2)	C55	C56	C57	126(2)
Au1	Au4	Au5	57.28(2)	C58	C57	C56	115(2)
Au1	Au4	Au10	57.28(2)	C57	C58	C59	119.1(19)
Au2	Au4	Au5	63.21(2)	C60	C59	C58	120(2)
Au3	Au4	Au2	60.55(2)	C59	C60	C55	120(2)
Au3	Au4	Au5	109.62(3)	C62	C61	P7	119.5(13)
Au3	Au4	Au10	99.74(3)	C66	C61	P7	119.9(14)
Au10	Au4	Au2	111.60(3)	C66	C61	C62	120.6(17)
Au10	Au4	Au5	66.18(2)	C63	C62	C61	118.0(18)

P4	Au4	Au1	171.57(12)	C64	C63	C62	122(2)
P4	Au4	Au2	130.80(12)	C63	C64	C65	120(2)
P4	Au4	Au3	123.20(12)	C66	C65	C64	121(2)
P4	Au4	Au5	124.79(12)	C65	C66	C61	118.8(19)
P4	Au4	Au10	115.09(11)	C68	C67	P7	116.8(14)
Au1	Au5	Au2	55.94(2)	C72	C67	P7	122.0(17)
Au1	Au5	Au4	58.10(2)	C72	C67	C68	121(2)
Au1	Au5	Au6	56.67(2)	C69	C68	C67	118(2)
Au1	Au5	Au10	53.88(2)	C70	C69	C68	120(2)
Au1	Au5	Au11	56.67(2)	C69	C70	C71	122(2)
Au2	Au5	Au10	100.35(3)	C72	C71	C70	118(2)
Au4	Au5	Au2	57.99(2)	C73	P8	Au8	116.1(6)
Au4	Au5	Au6	106.54(3)	C73	P8	C79	101.8(8)
Au4	Au5	Au10	56.18(2)	C73	P8	C85	101.0(8)
Au4	Au5	Au11	103.99(3)	C79	P8	Au8	114.8(7)
Au6	Au5	Au2	59.78(2)	C85	P8	Au8	114.5(6)
Au6	Au5	Au10	103.94(3)	C85	P8	C79	107.0(8)
Au11	Au5	Au2	107.26(3)	C71	C72	C67	122(2)
Au11	Au5	Au6	62.89(2)	C74	C73	P8	118.6(15)
Au11	Au5	Au10	55.95(2)	C78	C73	P8	125.4(15)
Cl5	Au5	Au1	178.94(13)	C78	C73	C74	115.7(19)
Cl5	Au5	Au2	125.12(12)	C73	C74	C75	122(2)
Cl5	Au5	Au4	122.23(14)	C76	C75	C74	121(2)
Cl5	Au5	Au6	123.63(14)	C75	C76	C77	115(2)
Cl5	Au5	Au10	125.30(13)	C76	C77	C78	123(2)
Cl5	Au5	Au11	122.40(12)	C73	C78	C77	122(2)
Au1	Au6	Au2	56.74(2)	C80	C79	P8	115.8(15)
Au1	Au6	Au5	57.16(2)	C84	C79	P8	123.1(15)
Au1	Au6	Au7	56.39(2)	C84	C79	C80	121.1(18)
Au1	Au6	Au8	50.43(2)	C81	C80	C79	120(2)
Au1	Au6	Au11	55.16(2)	C80	C81	C82	119(2)

Au2	Au6	Au7	60.70(2)	C83	C82	C81	122(2)
Au2	Au6	Au8	100.02(3)	C82	C83	C84	118(2)
Au2	Au6	Au11	105.32(3)	C79	C84	C83	120(2)
Au5	Au6	Au2	61.55(2)	C86	C85	P8	123.0(15)
Au5	Au6	Au7	107.72(3)	C86	C85	C90	120.0(18)
Au5	Au6	Au8	98.86(3)	C90	C85	P8	116.7(14)
Au5	Au6	Au11	58.52(2)	C85	C86	C87	120(2)
Au7	Au6	Au8	54.92(2)	C88	C87	C86	119(2)
Au7	Au6	Au11	101.13(3)	C89	C88	C87	121(2)
Au11	Au6	Au8	53.36(2)	C88	C89	C90	121(2)
P6	Au6	Au1	175.04(14)	C91	P9	Au9	114.2(7)
P6	Au6	Au2	121.31(13)	C97	P9	Au9	115.9(7)
P6	Au6	Au5	117.92(13)	C97	P9	C91	103.8(11)
P6	Au6	Au7	127.50(13)	C103	P9	Au9	114.3(7)
P6	Au6	Au8	133.69(14)	C103	P9	C91	105.4(10)
P6	Au6	Au11	123.76(12)	C103	P9	C97	101.8(9)
Au1	Au7	Au2	56.06(2)	C85	C90	C89	119(2)
Au1	Au7	Au3	58.05(2)	C92	C91	P9	119.7(19)
Au1	Au7	Au6	55.96(2)	C92	C91	C96	121(2)
Au1	Au7	Au8	55.65(2)	C96	C91	P9	120(2)
Au3	Au7	Au2	58.38(2)	C91	C92	C93	118(3)
Au3	Au7	Au6	105.93(3)	C94	C93	C92	118(3)
Au3	Au7	Au8	98.54(3)	C95	C94	C93	122(3)
Au6	Au7	Au2	59.27(2)	C94	C95	C96	120(3)
Au8	Au7	Au2	109.02(3)	C95	C96	C91	120(3)
Au8	Au7	Au6	68.75(2)	C98	C97	P9	117.4(18)
P7	Au7	Au1	166.70(13)	C98	C97	C102	117(2)
P7	Au7	Au2	123.43(13)	C102	C97	P9	124.9(19)
P7	Au7	Au3	109.45(13)	C97	C98	C99	124(2)
P7	Au7	Au6	136.83(12)	C100	C99	C98	116(3)
P7	Au7	Au8	127.52(13)	C99	C100	C101	123(3)

Au1	Au8	Au6	51.51(2)	C102	C101	C100	120(2)
Au1	Au8	Au7	57.41(2)	C101	C102	C97	120(2)
Au1	Au8	Au9	53.69(2)	C104	C103	P9	119.3(15)
Au1	Au8	Au11	57.74(2)	C104	C103	C108	119.9(18)
Au7	Au8	Au6	56.33(2)	C108	C103	P9	120.9(15)
Au7	Au8	Au9	79.59(3)	C103	C104	C105	120.9(18)
Au9	Au8	Au6	104.86(3)	C104	C105	C106	120(2)
Au11	Au8	Au6	58.18(2)	C107	C106	C105	120(2)
Au11	Au8	Au7	106.55(3)	C106	C107	C108	121.5(19)
Au11	Au8	Au9	88.28(3)	C109	P10	Au10	116.3(6)
P8	Au8	Au1	178.20(13)	C109	P10	C115	103.6(8)
P8	Au8	Au6	127.49(13)	C109	P10	C121	103.5(9)
P8	Au8	Au7	123.68(13)	C115	P10	Au10	112.3(6)
P8	Au8	Au9	127.47(13)	C121	P10	Au10	112.8(7)
P8	Au8	Au11	120.53(13)	C121	P10	C115	107.4(8)
Au1	Au9	Au3	58.62(2)	C103	C108	C107	118.4(19)
Au1	Au9	Au8	53.91(2)	C110	C109	P10	118.9(16)
Au1	Au9	Au10	55.69(2)	C110	C109	C114	117(2)
Au3	Au9	Au8	94.64(3)	C114	C109	P10	123.6(15)
Au3	Au9	Au10	94.41(3)	C109	C110	C111	121(2)
Au10	Au9	Au8	86.61(3)	C110	C111	C112	123(2)
P9	Au9	Au1	175.81(14)	C111	C112	C113	117(2)
P9	Au9	Au3	117.36(14)	C114	C113	C112	119(2)
P9	Au9	Au8	127.24(15)	C113	C114	C109	123(2)
P9	Au9	Au10	127.41(14)	C116	C115	P10	120.9(14)
Au1	Au10	Au4	58.97(2)	C120	C115	P10	118.3(14)
Au1	Au10	Au5	54.63(2)	C120	C115	C116	120.6(17)
Au1	Au10	Au9	54.52(2)	C115	C116	C117	120.8(18)
Au1	Au10	Au11	57.94(2)	C118	C117	C116	118.3(19)
Au4	Au10	Au5	57.64(2)	C117	C118	C119	121(2)
Au4	Au10	Au9	80.17(3)	C120	C119	C118	120(2)

Au4	Au10	Au11	107.36(3)	C115	C120	C119	119(2)
Au9	Au10	Au5	108.63(3)	C122	C121	P10	116.6(16)
Au11	Au10	Au5	58.43(2)	C122	C121	C126	122.2(19)
Au11	Au10	Au9	90.58(3)	C126	C121	P10	121.1(16)
P10	Au10	Au1	174.64(12)	C121	C122	C123	122(3)
P10	Au10	Au4	122.50(13)	C122	C123	C124	117(3)
P10	Au10	Au5	121.05(13)	C123	C124	C125	122(3)
P10	Au10	Au9	130.16(13)	C126	C125	C124	117(3)
P10	Au10	Au11	117.59(12)	C127	P11	Au11	116.5(6)
Au1	Au11	Au5	57.20(2)	C133	P11	Au11	116.3(7)
Au1	Au11	Au6	55.20(2)	C133	P11	C127	105.9(9)
Au1	Au11	Au8	56.43(2)	C133	P11	C139	102.1(9)
Au1	Au11	Au10	57.63(2)	C139	P11	Au11	112.4(6)
Au5	Au11	Au6	58.59(2)	C139	P11	C127	101.7(9)
Au8	Au11	Au5	110.42(3)	C125	C126	C121	119(2)
Au8	Au11	Au6	68.46(2)	C128	C127	P11	116.3(16)
Au10	Au11	Au5	65.62(3)	C132	C127	P11	121.9(17)
Au10	Au11	Au6	107.92(3)	C132	C127	C128	122(2)
Au10	Au11	Au8	94.51(3)	C127	C128	C129	118(2)
P11	Au11	Au1	177.27(13)	C130	C129	C128	121(2)
P11	Au11	Au5	124.96(13)	C129	C130	C131	119(2)
P11	Au11	Au6	127.02(13)	C132	C131	C130	121(2)
P11	Au11	Au8	122.14(13)	C127	C132	C131	119(2)
P11	Au11	Au10	121.09(13)	C134	C133	P11	115.6(14)
C1	P2	Au2	111.6(6)	C138	C133	P11	124.8(17)
C7	P2	Au2	113.8(6)	C138	C133	C134	119.5(18)
C7	P2	C1	106.3(8)	C133	C134	C135	117.8(17)
C7	P2	C13	103.2(9)	C136	C135	C134	121(2)
C13	P2	Au2	116.7(6)	C135	C136	C137	118(2)
C13	P2	C1	104.2(8)	C138	C137	C136	122(2)
C2	C1	P2	118.5(14)	C137	C138	C133	121(2)

C2	C1	C6	119.8(18)	C140	C139	P11	119.8(15)
C6	C1	P2	121.8(16)	C140	C139	C144	119.7(17)
C1	C2	C3	120.6(19)	C144	C139	P11	120.2(14)
C4	C3	C2	120(2)	C141	C140	C139	119.3(18)
C5	C4	C3	119.6(19)	C140	C141	C142	121.4(19)
C4	C5	C6	121.4(19)	C141	C142	C143	121(2)
C1	C6	C5	118.5(19)	C142	C143	C144	119.2(19)
C8	C7	P2	122.8(14)	C143	C144	C139	119.7(18)
C12	C7	P2	118.2(14)	Cl51	C500	Cl50	121(3)
C12	C7	C8	119.0(18)				

Table SI 7: Bond Lengths for Au₈.

Atom Atom Length/Å			Atom Atom Length/Å		
Au1	Au2	2.8748(6)	C57	C58	1.387(19)
Au1	Au3	2.8701(6)	C58	C59	1.391(16)
Au1	Au4	2.8852(6)	C59	C60	1.393(15)
Au1	Au6	2.7318(5)	C61	C62	1.444(16)
Au1	P7	2.322(3)	C61	C66	1.422(17)
Au2	Au6	2.7290(5)	C62	C63	1.343(17)
Au2	Au7	2.8882(6)	C63	C64	1.383(19)
Au2	P5	2.317(3)	C64	C65	1.326(18)
Au3	Au5	2.8664(5)	C65	C66	1.377(18)
Au3	Au6	2.6828(6)	C67	C68	1.374(16)
Au3	P3	2.290(3)	C67	C72	1.391(13)
Au4	Au5	2.8777(6)	C68	C69	1.412(13)
Au4	Au6	2.5827(6)	C69	C70	1.365(15)
Au4	Au7	2.8925(7)	C70	C71	1.408(18)
Au4	P4	2.260(3)	C71	C72	1.348(13)
Au5	Au6	2.7950(6)	C73	C74	1.402(12)
Au5	Au8	2.8723(7)	C73	C78	1.416(15)
Au5	P2	2.339(3)	C74	C75	1.370(14)

Au6	Au7	2.7352(6)	C75	C76	1.410(17)
Au6	Au8	2.6783(5)	C76	C77	1.379(14)
Au6	P1	2.382(3)	C77	C78	1.389(15)
Au7	Au8	2.8453(6)	C79	C80	1.391(15)
Au7	P6	2.316(3)	C79	C84	1.355(14)
Au8	P8	2.290(3)	C80	C81	1.360(14)
P1	C73	1.833(10)	C81	C82	1.370(15)
P1	C79	1.860(9)	C82	C83	1.367(16)
P1	C85	1.841(10)	C83	C84	1.397(14)
P2	C37	1.764(12)	C85	C86	1.389(15)
P2	C43	1.850(10)	C85	C90	1.392(14)
P2	C49	1.843(11)	C86	C87	1.365(16)
P3	C55	1.818(12)	C87	C88	1.385(15)
P3	C61	1.760(12)	C88	C89	1.400(16)
P3	C67	1.845(9)	C89	C90	1.379(15)
P4	C126	1.794(9)	C91	C92	1.378(16)
P4	C132	1.853(11)	C91	C96	1.376(16)
P4	C137	1.826(12)	C92	C93	1.371(16)
P5	C91	1.814(11)	C93	C94	1.392(18)
P5	C97	1.804(12)	C94	C95	1.378(18)
P5	C103	1.833(11)	C95	C96	1.383(17)
P6	C1	1.857(10)	C97	C98	1.399(16)
P6	C7	1.822(11)	C97	C102	1.358(14)
P6	C13	1.805(11)	C98	C99	1.400(17)
P7	C109	1.784(11)	C99	C100	1.350(16)
P7	C115	1.792(10)	C100	C101	1.36(2)
P7	C121	1.810(13)	C101	C102	1.419(18)
P8	C19	1.831(12)	C103	C104	1.402(16)
P8	C30	1.793(12)	C103	C108	1.390(15)
P8	C31	1.790(11)	C104	C105	1.393(15)
C1	C2	1.316(15)	C105	C106	1.330(17)

C1	C6	1.386(14)	C106	C107	1.396(17)
C2	C3	1.358(14)	C107	C108	1.348(16)
C3	C4	1.442(16)	C109	C110	1.341(14)
C4	C5	1.315(17)	C109	C114	1.439(13)
C5	C6	1.396(15)	C110	C111	1.398(17)
C7	C8	1.439(15)	C111	C112	1.422(15)
C7	C12	1.332(17)	C112	C113	1.368(15)
C8	C9	1.376(16)	C113	C114	1.385(17)
C9	C10	1.388(18)	C115	C116	1.430(13)
C10	C11	1.408(18)	C115	C120	1.403(16)
C11	C12	1.395(17)	C116	C117	1.350(15)
C13	C14	1.424(16)	C117	C118	1.394(19)
C13	C18	1.368(14)	C118	C119	1.378(15)
C14	C15	1.360(16)	C119	C120	1.368(15)
C15	C16	1.352(14)	C121	C122	1.319(17)
C16	C17	1.408(18)	C121	C142	1.377(17)
C17	C18	1.348(17)	C122	C123	1.377(19)
C19	C20	1.402(16)	C123	C124	1.38(2)
C19	C24	1.381(17)	C124	C125	1.336(18)
C20	C21	1.347(17)	C125	C142	1.381(19)
C21	C22	1.336(18)	C126	C127	1.358(16)
C22	C23	1.351(18)	C126	C131	1.428(13)
C23	C24	1.423(19)	C127	C128	1.397(14)
C25	C26	1.438(17)	C128	C129	1.400(15)
C25	C30	1.401(15)	C129	C130	1.381(17)
C26	C27	1.352(17)	C130	C131	1.379(14)
C27	C28	1.412(17)	C132	C133	1.353(17)
C28	C29	1.399(17)	C132	C136	1.364(16)
C29	C30	1.398(16)	C133	C134	1.376(17)
C31	C32	1.418(13)	C134	C143	1.380(18)
C31	C36	1.360(16)	C135	C136	1.404(17)

C32	C33	1.374(16)	C135	C143	1.35(2)
C33	C34	1.36(2)	C137	C138	1.385(15)
C34	C35	1.385(15)	C137	C144	1.386(15)
C35	C36	1.420(16)	C138	C139	1.324(16)
C37	C38	1.416(17)	C139	C140	1.392(15)
C37	C42	1.426(16)	C140	C141	1.351(19)
C38	C39	1.293(18)	C141	C144	1.379(19)
C39	C40	1.413(19)	N11	O11	1.3827(13)
C40	C41	1.32(2)	N11	O12	1.0899(12)
C41	C42	1.461(19)	N11	O13	1.2000(9)
C43	C44	1.395(16)	N21	O21	1.3831(13)
C43	C48	1.342(15)	N21	O22	1.0896(13)
C44	C45	1.436(15)	N21	O23	1.2000(2)
C45	C46	1.356(16)	C550	Cl50	1.611(10)
C46	C47	1.368(18)	C550	Cl51	1.709(9)
C47	C48	1.372(15)	C510	Cl10	1.588(13)
C49	C50	1.359(12)	C510	Cl11	1.698(11)
C49	C54	1.316(15)	C520	Cl20	1.95(2)
C50	C51	1.387(17)	C520	Cl21	1.51(2)
C51	C52	1.408(18)	C530	Cl30	1.562(13)
C52	C53	1.319(15)	C530	Cl31	1.677(14)
C53	C54	1.500(18)	C540	Cl40	1.609(11)
C55	C56	1.377(14)	C540	Cl41	1.714(12)
C55	C60	1.342(15)	C560	Cl60	1.64(2)
C56	C57	1.410(17)	C560	Cl61	1.79(2)

Table SI 8: Bond Angles for Au₈.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Au2	Au1	Au4	87.525(17)	C29	C28	C27	121.9(12)
Au3	Au1	Au2	108.069(19)	C30	C29	C28	119.3(11)
Au3	Au1	Au4	79.629(15)	C25	C30	P8	117.6(9)

Au6	Au1	Au2	58.188(14)	C29	C30	P8	122.2(9)
Au6	Au1	Au3	57.164(14)	C29	C30	C25	120.2(11)
Au6	Au1	Au4	54.666(14)	C32	C31	P8	121.2(9)
P7	Au1	Au2	118.95(8)	C36	C31	P8	121.0(7)
P7	Au1	Au3	124.81(8)	C36	C31	C32	117.8(10)
P7	Au1	Au4	127.03(8)	C33	C32	C31	120.1(12)
P7	Au1	Au6	177.06(8)	C34	C33	C32	122.1(11)
Au1	Au2	Au7	92.824(17)	C33	C34	C35	119.3(12)
Au6	Au2	Au1	58.282(14)	C34	C35	C36	119.1(12)
Au6	Au2	Au7	58.196(15)	C31	C36	C35	121.5(9)
P5	Au2	Au1	130.37(7)	C38	C37	P2	120.4(9)
P5	Au2	Au6	163.41(8)	C38	C37	C42	117.3(11)
P5	Au2	Au7	127.92(8)	C42	C37	P2	121.5(9)
Au5	Au3	Au1	99.995(19)	C39	C38	C37	120.8(13)
Au6	Au3	Au1	58.823(15)	C38	C39	C40	124.1(14)
Au6	Au3	Au5	60.379(15)	C41	C40	C39	118.5(14)
P3	Au3	Au1	126.12(6)	C40	C41	C42	120.7(15)
P3	Au3	Au5	126.77(6)	C37	C42	C41	118.4(12)
P3	Au3	Au6	164.34(8)	C44	C43	P2	120.7(8)
Au1	Au4	Au7	92.518(17)	C48	C43	P2	119.6(9)
Au5	Au4	Au1	99.372(19)	C48	C43	C44	119.6(10)
Au5	Au4	Au7	100.303(18)	C43	C44	C45	115.6(11)
Au6	Au4	Au1	59.642(15)	C46	C45	C44	123.5(12)
Au6	Au4	Au5	61.295(16)	C45	C46	C47	118.2(10)
Au6	Au4	Au7	59.624(17)	C46	C47	C48	119.4(12)
P4	Au4	Au1	118.51(7)	C43	C48	C47	123.6(12)
P4	Au4	Au5	118.73(8)	C50	C49	P2	120.8(9)
P4	Au4	Au6	177.85(8)	C54	C49	P2	116.9(8)
P4	Au4	Au7	122.13(9)	C54	C49	C50	122.1(11)
Au3	Au5	Au4	79.815(15)	C49	C50	C51	122.7(11)
Au3	Au5	Au8	109.697(18)	C50	C51	C52	116.9(10)

Au6	Au5	Au3	56.554(14)	C53	C52	C51	120.6(13)
Au6	Au5	Au4	54.142(14)	C52	C53	C54	120.9(12)
Au6	Au5	Au8	56.386(14)	C49	C54	C53	116.2(9)
Au8	Au5	Au4	78.043(17)	C56	C55	P3	123.7(9)
P2	Au5	Au3	119.03(8)	C60	C55	P3	116.6(8)
P2	Au5	Au4	131.77(8)	C60	C55	C56	119.7(10)
P2	Au5	Au6	173.29(9)	C55	C56	C57	119.0(11)
P2	Au5	Au8	125.34(7)	C58	C57	C56	120.4(12)
Au1	Au6	Au5	105.321(19)	C57	C58	C59	119.0(12)
Au1	Au6	Au7	99.553(18)	C58	C59	C60	118.5(12)
Au2	Au6	Au1	63.530(15)	C55	C60	C59	122.8(10)
Au2	Au6	Au5	161.69(2)	C62	C61	P3	125.1(9)
Au2	Au6	Au7	63.817(15)	C66	C61	P3	121.0(9)
Au3	Au6	Au1	64.013(16)	C66	C61	C62	113.9(11)
Au3	Au6	Au2	118.447(17)	C63	C62	C61	121.7(12)
Au3	Au6	Au5	63.067(15)	C62	C63	C64	121.1(13)
Au3	Au6	Au7	154.28(2)	C65	C64	C63	120.3(13)
Au4	Au6	Au1	65.692(16)	C64	C65	C66	120.8(13)
Au4	Au6	Au2	97.149(19)	C65	C66	C61	122.2(13)
Au4	Au6	Au3	88.81(2)	C68	C67	P3	121.6(7)
Au4	Au6	Au5	64.563(17)	C68	C67	C72	120.5(9)
Au4	Au6	Au7	65.828(18)	C72	C67	P3	117.8(8)
Au4	Au6	Au8	86.945(18)	C67	C68	C69	118.7(10)
Au7	Au6	Au5	106.457(18)	C70	C69	C68	120.3(12)
Au8	Au6	Au1	152.34(2)	C69	C70	C71	119.7(10)
Au8	Au6	Au2	119.34(2)	C72	C71	C70	120.0(10)
Au8	Au6	Au3	122.144(19)	C71	C72	C67	120.7(11)
Au8	Au6	Au5	63.265(15)	C74	C73	P1	119.5(8)
Au8	Au6	Au7	63.406(16)	C74	C73	C78	119.2(9)
P1	Au6	Au1	120.15(6)	C78	C73	P1	121.3(7)
P1	Au6	Au2	87.68(6)	C75	C74	C73	120.8(11)

P1	Au6	Au3	92.25(7)	C74	C75	C76	119.4(9)
P1	Au6	Au4	173.84(6)	C77	C76	C75	120.7(10)
P1	Au6	Au5	110.62(6)	C76	C77	C78	120.2(11)
P1	Au6	Au7	113.42(7)	C77	C78	C73	119.6(9)
P1	Au6	Au8	87.35(6)	C80	C79	P1	117.9(8)
Au2	Au7	Au4	87.132(17)	C84	C79	P1	123.3(8)
Au6	Au7	Au2	57.987(14)	C84	C79	C80	118.6(9)
Au6	Au7	Au4	54.548(16)	C81	C80	C79	120.2(10)
Au6	Au7	Au8	57.322(14)	C80	C81	C82	121.9(11)
Au8	Au7	Au2	108.98(2)	C83	C82	C81	117.9(10)
Au8	Au7	Au4	78.236(17)	C82	C83	C84	120.9(11)
P6	Au7	Au2	122.46(7)	C79	C84	C83	120.4(12)
P6	Au7	Au4	122.16(9)	C86	C85	P1	120.8(8)
P6	Au7	Au6	176.62(9)	C86	C85	C90	117.5(10)
P6	Au7	Au8	123.91(6)	C90	C85	P1	121.6(8)
Au6	Au8	Au5	60.350(15)	C87	C86	C85	122.4(11)
Au6	Au8	Au7	59.271(15)	C86	C87	C88	119.7(12)
Au7	Au8	Au5	101.572(18)	C87	C88	C89	119.3(11)
P8	Au8	Au5	126.15(8)	C90	C89	C88	119.8(10)
P8	Au8	Au6	166.88(9)	C89	C90	C85	121.1(11)
P8	Au8	Au7	124.23(8)	C92	C91	P5	119.6(9)
C73	P1	Au6	118.0(3)	C96	C91	P5	123.9(9)
C73	P1	C79	100.1(5)	C96	C91	C92	116.5(11)
C73	P1	C85	102.9(5)	C93	C92	C91	121.9(12)
C79	P1	Au6	117.7(3)	C92	C93	C94	119.8(13)
C85	P1	Au6	113.9(4)	C95	C94	C93	120.0(13)
C85	P1	C79	101.8(5)	C94	C95	C96	117.7(13)
C37	P2	Au5	115.2(3)	C91	C96	C95	123.9(12)
C37	P2	C43	101.5(5)	C98	C97	P5	118.8(8)
C37	P2	C49	106.6(5)	C102	C97	P5	122.9(10)
C43	P2	Au5	119.4(4)	C102	C97	C98	118.3(11)

C49	P2	Au5	111.7(3)	C97	C98	C99	118.5(10)
C49	P2	C43	100.7(5)	C100	C99	C98	123.4(13)
C55	P3	Au3	113.8(4)	C99	C100	C101	117.9(13)
C55	P3	C67	102.9(5)	C100	C101	C102	120.5(12)
C61	P3	Au3	115.7(4)	C97	C102	C101	121.2(12)
C61	P3	C55	105.8(5)	C104	C103	P5	122.7(9)
C61	P3	C67	104.2(5)	C108	C103	P5	118.7(9)
C67	P3	Au3	113.1(3)	C108	C103	C104	118.3(10)
C126	P4	Au4	112.8(4)	C105	C104	C103	119.2(11)
C126	P4	C132	104.4(5)	C106	C105	C104	121.4(12)
C126	P4	C137	104.7(5)	C105	C106	C107	119.6(11)
C132	P4	Au4	112.5(4)	C108	C107	C106	120.6(12)
C137	P4	Au4	116.8(4)	C107	C108	C103	120.7(12)
C137	P4	C132	104.5(5)	C110	C109	P7	123.6(8)
C91	P5	Au2	114.4(3)	C110	C109	C114	115.7(10)
C91	P5	C103	102.8(5)	C114	C109	P7	120.6(8)
C97	P5	Au2	114.4(4)	C109	C110	C111	124.9(10)
C97	P5	C91	105.1(6)	C110	C111	C112	117.9(10)
C97	P5	C103	103.6(5)	C113	C112	C111	118.8(11)
C103	P5	Au2	115.1(4)	C112	C113	C114	121.0(10)
C1	P6	Au7	112.8(4)	C113	C114	C109	121.2(10)
C7	P6	Au7	118.4(4)	C116	C115	P7	122.9(9)
C7	P6	C1	98.3(5)	C120	C115	P7	119.6(7)
C13	P6	Au7	113.8(4)	C120	C115	C116	117.0(9)
C13	P6	C1	107.9(5)	C117	C116	C115	120.5(12)
C13	P6	C7	104.0(5)	C116	C117	C118	121.0(11)
C109	P7	Au1	117.4(3)	C119	C118	C117	119.6(11)
C109	P7	C115	104.7(5)	C120	C119	C118	120.2(13)
C109	P7	C121	103.1(5)	C119	C120	C115	121.6(10)
C115	P7	Au1	110.8(4)	C122	C121	P7	126.1(11)
C115	P7	C121	104.4(5)	C122	C121	C142	115.4(13)

C121	P7	Au1	115.1(3)	C142	C121	P7	118.4(9)
C19	P8	Au8	111.2(4)	C121	C122	C123	125.6(13)
C30	P8	Au8	116.6(3)	C124	C123	C122	117.9(13)
C30	P8	C19	105.7(5)	C125	C124	C123	118.3(13)
C31	P8	Au8	115.0(4)	C124	C125	C142	121.6(14)
C31	P8	C19	103.9(5)	C127	C126	P4	123.5(8)
C31	P8	C30	103.2(5)	C127	C126	C131	118.4(9)
C2	C1	P6	124.2(7)	C131	C126	P4	118.0(8)
C2	C1	C6	119.2(9)	C126	C127	C128	122.3(10)
C6	C1	P6	116.5(9)	C127	C128	C129	119.0(11)
C1	C2	C3	120.4(10)	C130	C129	C128	119.2(10)
C2	C3	C4	119.9(12)	C131	C130	C129	121.5(10)
C5	C4	C3	119.8(10)	C130	C131	C126	119.5(11)
C4	C5	C6	117.7(11)	C133	C132	P4	118.0(8)
C1	C6	C5	122.4(11)	C133	C132	C136	119.5(11)
C8	C7	P6	121.3(9)	C136	C132	P4	122.4(10)
C12	C7	P6	120.6(8)	C132	C133	C134	122.8(12)
C12	C7	C8	118.1(11)	C133	C134	C143	117.8(13)
C9	C8	C7	119.3(12)	C143	C135	C136	121.0(13)
C8	C9	C10	120.9(12)	C132	C136	C135	118.7(13)
C9	C10	C11	119.7(13)	C138	C137	P4	123.9(8)
C12	C11	C10	117.5(13)	C138	C137	C144	119.2(11)
C7	C12	C11	124.0(12)	C144	C137	P4	116.8(9)
C14	C13	P6	121.6(8)	C139	C138	C137	121.2(10)
C18	C13	P6	119.0(9)	C138	C139	C140	120.8(12)
C18	C13	C14	119.0(10)	C141	C140	C139	118.3(13)
C15	C14	C13	119.7(10)	C140	C141	C144	122.3(12)
C16	C15	C14	120.7(12)	C121	C142	C125	121.1(13)
C15	C16	C17	119.6(11)	C135	C143	C134	120.2(13)
C18	C17	C16	120.5(11)	C141	C144	C137	118.0(12)
C17	C18	C13	120.5(12)	O12	N11	O11	116.07(12)

C20	C19	P8	118.8(9)	O12	N11	O13	138.71(14)
C24	C19	P8	122.3(10)	O13	N11	O11	102.55(11)
C24	C19	C20	118.8(12)	O22	N21	O21	116.04(14)
C21	C20	C19	121.5(12)	O22	N21	O23	138.79(19)
C22	C21	C20	120.8(13)	O23	N21	O21	102.51(12)
C21	C22	C23	119.9(13)	Cl50	C550	Cl51	119.9(7)
C22	C23	C24	122.2(14)	Cl10	C510	Cl11	119.9(8)
C19	C24	C23	116.7(13)	Cl21	C520	Cl20	109.7(11)
C30	C25	C26	118.3(11)	Cl30	C530	Cl31	125.1(10)
C27	C26	C25	122.4(12)	Cl40	C540	Cl41	118.8(9)
C26	C27	C28	117.9(12)	Cl60	C560	Cl61	114.4(13)

References

- (1) *Handbook of Preparative Inorganic Chemistry* Brauer, G., Ed.; Academic Press: NY., 1963; Vol. 1.
- (2) Malatesta, L.; Naldini, L.; Simonetta, G.; Cariati, F. *Coordination Chemistry Reviews* **1966**, *1*, 255.
- (3) Mueting, A. M.; Alexander, B. D.; Boyle, P. D.; Ito, L. N.; Johnson, B. J.; Pignolet, L. H. *Inorganic Syntheses*; John Wiley and Sons, Inc, 1992; Vol. 29.
- (4) Weare, W. W.; Reed, S. M.; Warner, M. G.; Hutchison, J. E. *Journal of the American Chemical Society* **2000**, *122*, 12890.
- (5) Woehrle, G. H.; Warner, M. G.; Hutchison, J. E. *The Journal of Physical Chemistry B* **2002**, *106*, 9979.
- (6) McKenzie, L. C., University of Oregon, 2009.
- (7) Wen, F.; Englert, U.; Gutrath, B.; Simon, U. *European Journal of Inorganic Chemistry* **2008**, *2008*, 106.
- (8) Van der Velden, J. W. A.; Bour, J. J.; Bosman, W. P.; Noordik, J. H. *Inorganic Chemistry* **1983**, *22*, 1913.
- (9) Lopez-Sanchez, J.; Dimitratos, N.; Hammond, C.; Brett, G.; Kesavan, L.; White, S.; Miedziak, P.; Tiruvalam, R.; Jenkins, R.; Carley, A.; Knight, D.; Kiely, C.; Hutchings, G. *Nature chemistry* **2011**, *3*, 551.
- (10) Sheldrick, G. M. *Acta Crystallographica Section A* **2008**, *64*, 112.
- (11) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *Journal of Applied Crystallography* **2009**, *42*, 339.
- (12) Hirshfeld, F. *Acta Crystallographica Section A* **1976**, *32*, 239.